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ORIGINAL ARTICLE

Silica sulfuric acid-coated Fe_3O_4 nanoparticles as high reusable nanocatalyst for the oxidation of sulfides into sulfoxides, protection and deprotection of hydroxyl groups using HMDS and Ac_2O

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KEYWORDS

Magnetic nanoparticles;
Silica sulfuric acid;
Sulfide;
Alcohol;
Sulfoxide;
Trimethylsilylation;
Acetylation

Abstract Oxidation of sulfides, acetylation of alcohols and phenols and selective trimethylsilylation of primary and secondary benzyl alcohols are carried out using silica sulfuric acid-coated Fe_3O_4 magnetic nanoparticles (SSA@MNPs) as a stable, efficient and magnetically recoverable nanocatalyst. Also, deprotection of silyl ethers was reported in ethanol at room temperature in the presence of SSA@MNPs as a magnetic nanocatalyst. The magnetic nanocatalyst was characterized by FT-IR spectroscopy, TGA, XRD and SEM techniques. The catalyst was easily separated with the assistance of an external magnetic field from the reaction mixture and reused for several consecutive runs without significant loss of its catalytic efficiency.

1. Introduction

During the past two decades, a great deal of attention has been paid to developing methods for heterogenizing homogeneous catalysts in order to combine the advantages of both homogeneous and heterogeneous catalyses [1,2]. Nanoparticulate supports can serve to bridge the gap between these two traditional disciplines [3]. However, the nanocatalyst supported can be separated from products by conventional filtration or centrifugation techniques. But, it is difficult, time consuming and expensive to separate fine particles from a reaction mixture [4]. Therefore, magnetic nanoparticles (MNPs) based on iron oxides have emerged in the organic reactions, which can be easily and rapidly isolated from the reaction mixture using external magnet [5]. More importantly, magnetic separation of the MNPs is easier and more effective than filtration or centrifugation [6,7]. However, bare nanoparticles of iron oxides tend to aggregate into large clusters and lose their catalyst

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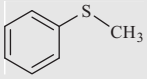
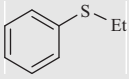
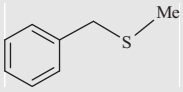
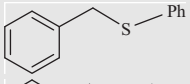
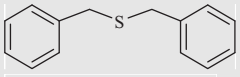
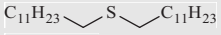
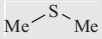
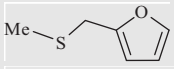
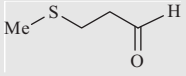
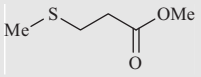
Table 1 Optimization of the reaction conditions for the oxidation of benzyl methyl sulfide (1 mmol) as a model compound.

Entry	Solvent	Catalyst (mg)	H_2O_2 (mmol)	Time (min)	Conversion (%)
1	CH_3CN	5	1.2	24	100
2	CH_2Cl_2	5	1.2	10	100
3	Ethanol	5	1.2	25	100
4	*n*-Hexane	5	1.2	8	100
5	Solvent free	5	1.2	35	100
6	THF	5	1.2	60	Trace
7	Ethyl acetate	5	1.2	5	100
8	H_2O	15	1.2	5	100
9	H_2O	10	1.2	5	100
10	H_2O	5	1.2	13	100
11	H_2O	3	1.2	20	–[a]
12	H_2O	5	1.4	5	100
13	H_2O	5	1	30	100

[a] The reaction was not complete.

Table 2 Oxidation of sulfides into sulfoxides using H_2O_2 under the influence of SSA@MNPs in water and at room temperature.

Entry	Sulfide	Product	Time (min)	Yield (%)[a]
1		2a	5	87
2		2b	5	90
3		2c	13	87
4		2d	5	85
5		2e	5	92
6		2f	20	86
7		2g	10	91
8		2h	20	83
9		2i	10	87
10		2j	2	80
11		2k	15	97

[a] Isolated yield.

loading capacity when compared to many conventional single-nanoparticles [8]. On the other hand, it is also difficult to graft the surface of Fe_3O_4 MNPs with organic materials since there are few hydroxyl groups on the surface of Fe_3O_4 MNPs. Also to prevent the antioxidation of MNPs, the modification and surface coating for Fe_3O_4 MNPs is necessary [9]. Silica is commonly employed as the coating layer for the surface of MNPs because it is stable, inert, has a high specific surface area, non-toxic, surface modification is easy, cheap and resistant under catalytic conditions [10,11].

Table 3 Optimization of reaction conditions for trimethylsilylation of benzyl alcohol (1 mmol) with HMDS (1.5 mmol) as a model compound.

Entry	Solvent	Catalyst (mg)	Time (min)	Conversion (%)
1	CH_2Cl_2	10	100	–[a]
2	Solvent free	10	100	–[a]
3	THF	10	80	100
4	*n*-Hexane	10	100	–[a]
5	Ethyl acetate	10	100	–[a]
6	CH_3CN	15	10	100
7	CH_3CN	10	15	100
8	CH_3CN	5	20	100

[a] The reaction was not complete.

The selective oxidation of sulfides to sulfoxides is an important transformation in organic chemistry [12] because of their extensive applications as synthetic intermediates for the construction of various chemically, biologically active molecules and drug metabolism [13]. For example, omeprazole and the pesticide fipronil are two typical examples of the extensive application of these intermediates in pharmaceutical and fine chemical industries [14,15].

Besides, the protection–deprotection steps of active protic functional groups are frequently required in the multistep synthesis as well as in the chemistry of drug design and food or cosmetic industries [16]. Acetylation and trimethylsilylation of hydroxyl groups are the most widely used transformations for the protection of alcohols and phenols. Because acetylation and trimethylsilylation of hydroxyl groups are carried out under mild conditions, acetates and silyl ethers can also be easily deprotected into the parent hydroxyl groups [17,18]. On the other hand, silyl ethers have a good stability for most non-acidic reagents and non-polar solvents [19]. Furthermore, trimethylsilylation is also extensively used for the derivatization of hydroxyl compounds to increase their volatility for gas chromatography and mass spectrometry [19]. Respectively, acetylation and trimethylsilylation of hydroxyl groups are performed employing Ac_2O and 1,1,1,3,3,3-hexamethyldisilazane (HMDS) in the presence of protonic acids, Lewis acids, heteropoly acids, clays or amine bases [20–22].

2. Experimental

2.1. Preparation of catalyst

First, the Fe_3O_4 MNPs were prepared according to the very recently reported method [5–7]. Then the obtained Fe_3O_4 MNPs (2 g) were dispersed in 20 mL of water by sonication for 30 min, and then 2-propanol (200 mL) was added to the reaction mixture. The reaction mixture was stirred using a

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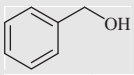
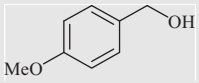
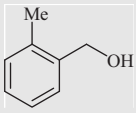
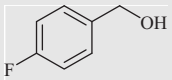
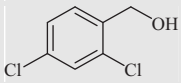
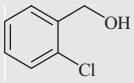
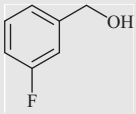
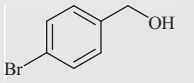
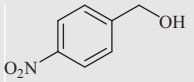
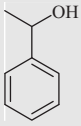
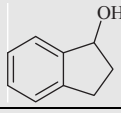
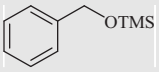
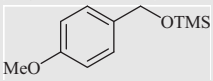
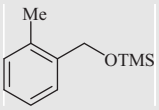
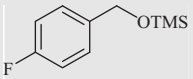
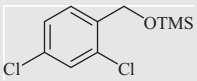
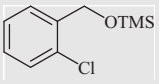
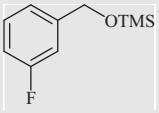
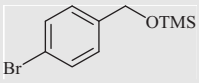
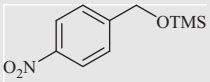
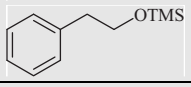
Table 4 Trimethylsilylation of benzylic alcohols using HMDS in the influence of SSA@MNPs.

Entry	Alcohol	Product	Time (min)	Yield (%)[a]
1		4a	20	95
2		4b	30	95
3		4c	40	92
4		4d	60	94
5		4e	60	95
6		4f	50	92
7		4g	50	92
8		4h	30	95
9		4i	70	95
10		4k	50	93
11		4l	40	93

[a] Isolated yield.

Table 5 Deprotection of silyl ethers in the presence of SSA@MNPs in ethanol.

Entry	Silyl ethers	Product	Time (min)	Yield (%)[a]
1		3a	5	94
2		3b	3	93
3		3c	5	93
4		3d	3	94
5		3e	3	95
6		3f	5	92
7		3g	3	92
8		3h	5	92
9		3i	15	96
10		3j	3	90

[a] Isolated yield.

magnetic stirrer at room temperature. Under continuous stirring, PEG (5.36 g), water (20 mL), ammonia solution (10 mL, 28 wt.%) and 2 mL of tetraethyl orthosilicate (TEOS) were respectively added into the suspension, and continuously reacted for 38 h under stirring at room temperature. Then the products (SiO_2@MNPs) were isolated with an external magnet and washed two times with ethanol and distilled water. Ultimately, the SiO_2@MNPs (1 g) were dispersed in dry *n*-hexane (5 mL) using an ultrasonic bath for 20 min. Subsequently, chlorosulfuric acid (1 mL) was added drop wise over a period of 30 min and the mixture was stirred for 4 h at room temperature. Then, the final product was separated by magnetic decantation and washed twice by dry *n*-hexane, ethanol and *n*-hexane respectively. The product (SSA@MNPs) was stored in a refrigerator until use.

2.2. General procedure for the oxidation of sulfides to sulfoxides

A mixture of sulfide (1 mmol), hydrogen peroxide (1.2 mmol) and SSA@MNPs (0.005 g) was stirred at room temperature in H_2O (2 mL) and the progress of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was separated from the mixture by an external magnet (within 5 s) and the product was extracted with ethyl acetate (2 × 5 mL). The combined organic layers were washed with brine (10 mL) and dried over anhydrous Na_2SO_4 (1.5 g). Ethyl acetate was removed under reduced pressure to give the corresponding pure sulfoxide in most cases. Further purification was achieved by short-column chromatography on silica gel with EtOAc/*n*-hexane (1/10) as eluent. All the products are known and were characterized by ^{1}H NMR and compared with those of authentic samples [23] (see supporting information for selected spectra).

2.3. General procedure for the trimethylsilylation of benzylic alcohols

A mixture of benzylic alcohols (1 mmol), HMDS (1.5 mmol) and SSA@MNPs (0.005 g) was stirred at room temperature in CH_3CN (5 mL) and the progress of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was separated by an external magnet and the mixture was decanted. Then, the mixture was washed with water (5 mL) to destroy the extra amounts of HMDS and organic layer was

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Table 6 Optimization of reaction conditions for acetylation of benzyl alcohol (1 mmol) with Ac_2O as a model compound.

Entry	Solvent	Catalyst (mg)	Ac_2O (mmol)	Time (min)	Conversion (%)
1	CH_3CN	3	1.5	100	0
2	Ethyl acetate	3	1.5	100	0
3	CH_2Cl_2	3	1.5	100	0
4	*n*-Hexane	3	1.5	150	100
5	Solvent free	3	1.5	15	100
6	THF	3	1.5	100	0
7	Solvent free	15	5	5	100
8	Solvent free	10	5	5	100
9	Solvent free	5	5	5	100
10	Solvent free	5	4	5	100
11	Solvent free	5	3	5	100
12	Solvent free	5	2	5	100
13	Solvent free	5	1.5	5	100
14	Solvent free	5	1	100	–[a]
15	Solvent free	3	1.5	15	100

[a] The reaction was not complete.

Table 7 Acetylation of alcohols and phenols using Ac_2O in the presence of SSA@MNPs.

Entry	Alcohol	Product	Time (min)	Yield (%)[a]
1	Benzyl alcohol	5a	15	85
2	4-Fluoro-benzyl alcohol	5b	5	83
3	2-Methyl-benzyl alcohol	5c	15	85
4	4-Methoxy-benzyl alcohol	5d	20	93
5	2-Chloro-benzyl alcohol	5e	50	89
6	4-Nitro-benzyl alcohol	5f	20	80
7	2,4-Dichloro-benzyl alcohol	5g	20	84
8	3-Fluoro-benzyl alcohol	5h	5	92
9	1-Phenylethanol	5i	15	81
10	Benzhydrol	5j	5	77
11	2-Phenylethanol	5k	10	86
12	1-Octanol	5l	40	92
13	Cyclohexanol	5m	45	82
14	Menthol	5n	50	80
15	Phenol	5o	20	88
16	2,4-Dichlorophenol	5p	20	93
17	4-Methoxyphenol	5q	20	90
18	4-Bromophenol	5r	5	92
19	2-Pentanol	5s	15	93

[a] Isolated yield.

dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave the pure product without further purification. All products were characterized by a comparison of their spectral data (^{1}H NMR, IR spectroscopy) with those of authentic samples [24] (see supporting information for selected spectra).

2.4. General procedure for the deprotection of silyl ether derivatives

A mixture of silyl ethers (1 mmol) and SSA@MNPs (0.003 g) was stirred at room temperature in EtOH (5 mL) and the progress of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was separated by an external magnet and the mixture was decanted. The solvent was evaporated under reduced pressure to give the corresponding alcohols. All products were characterized by a comparison of their FT-IR spectra with parent benzylic alcohols.

2.5. General procedure for the acetylation of hydroxyl groups

A mixture of alcohol or phenol (1 mmol), Ac_2O (1.5 mmol) and SSA@MNPs (0.005 g) was stirred at room temperature under solvent-free conditions and the progress of the reaction was monitored by TLC. After completion, the reaction was quenched with water (5 mL), the catalyst was separated by an external magnet and the mixture was decanted. The product was extracted with CH_2Cl_2 (4 × 5 mL). The organic layer was dried over anhydrous Na_2SO_4 (1.5 g) and evaporated under reduced pressure. The pure product was obtained in most cases. Further purification was achieved by short-column chromatography on silica gel with EtOAc/*n*-hexane (1/2) as eluent. All products were known and characterized by comparison of their spectral data (^{1}H NMR, IR spectroscopy) with those of authentic samples [25] (see supporting information for selected spectral).

2.5.1. Selected spectral data of sulfoxides, trimethylsilyl ethers and acetate esters (benzyl methyl sulfoxide 2c (Table 2, entry 3)

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.47 (s, 3H), 3.95 (d, J = 17 Hz, 1H), 4.13 (d, J = 17 Hz, 1H), 7.35 (s, 5H) ppm.

2.5.2. Furfuryl methyl sulfoxide 2h (Table 2, entry 8)

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.57 (s, 3H), 4.06 (d, J = 14 Hz, 1H), 4.14 (d, J = 14 Hz, 1H), 6.44 (d, J = 3.2 Hz, 1H), 7.20–7.58 (m, 2H) ppm.

2.5.3. Methyl 3-(methyl propanoate) sulfoxide 2j (Table 2, entry 10)

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.86 (t, J = 7.6 Hz, 2H), 2.94 (s, 3H), 3.36 (t, J = 7.6 Hz, 2H), 3.75 (s, 3H) ppm.

2.5.4. Tetrahydrothiophene 1-oxide 2k (Table 2, entry 11)

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.24 (t, J = 7.6 Hz, 4H), 3.05 (t, J = 7.6 Hz, 4H) ppm.

2.5.5. Benzyl trimethylsilyl ether 4a (Table 4, entry 1)

IR (KBr) cm^{-1}: 2957, 1454, 1251, 843, 752. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.42 (s, 9H), 4.90 (s, 2H), 7.53 (s, 5H) ppm.

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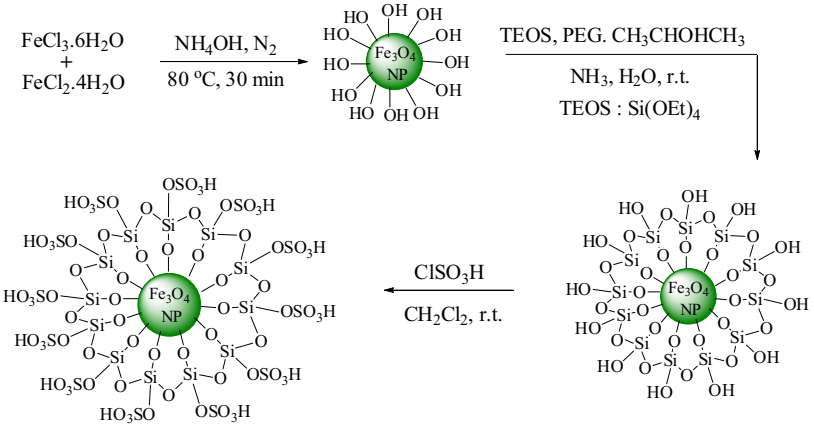

Scheme 1 Synthesis of SSA@MNPs.

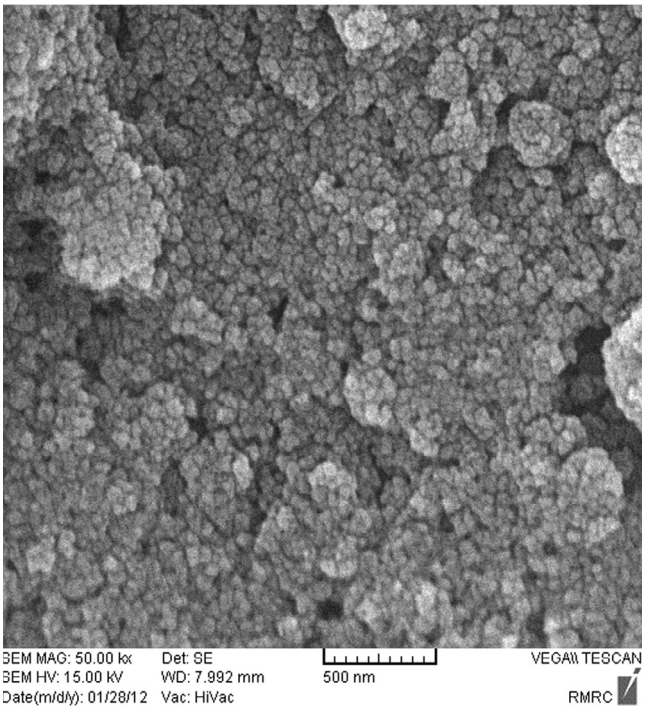

Figure 1 SEM images of SSA@MNPs.

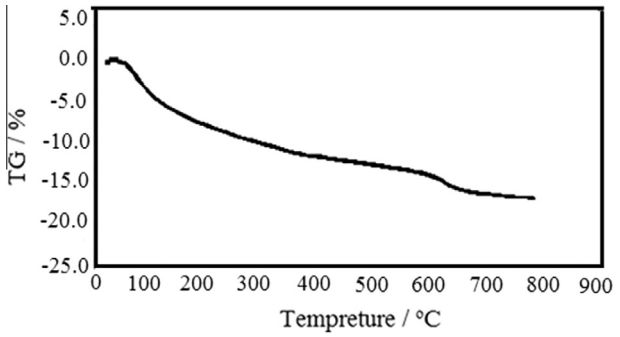

Figure 2 TGA diagram of SSA@MNPs.

2.5.6. 2,4-Dichlorobenzyl trimethylsilyl ether 4e (Table 4, entry 5)

IR (KBr) cm^{-1}: 2927, 1253, 846, 749. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.00 (s, 9H), 4.52 (s, 2H), 7.11 (m, 3H) ppm.

2.5.7. 4-Nitrobenzyl trimethylsilyl ether 4i (Table 4, entry 9)

IR (KBr) cm^{-1}: 2927, 1524, 1348, 1254, 847, 741. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.00 (s, 9H), 4.60 (s, 2H), 7.33 (d, J = 25 Hz, 2H), 7.90 (d, J = 25 Hz, 2H) ppm.

2.5.8. 4-Methoxybenzyl acetate 5d (Table 7, entry 4)

IR (KBr) cm^{-1}: 2854, 1743, 1378, 1245, 1034, 821. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.03 (s, 3H), 3.74 (S, 3H), 5.00 (s, 2H), 6.89 (d, J = 30 Hz, 2H), 7.22 (d, J = 30 Hz, 2H) ppm.

2.5.9. 4-Nitrobenzyl acetate 5f (Table 7, entry 6)

IR (KBr) cm^{-1}: 2853, 1740, 1719, 1519, 1462, 1377, 1344. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.08 (s, 3H), 5.13 (S, 2H), 7.49 (d, J = 20 Hz, 2H), 8.11 (d, J = 20 Hz, 2H) ppm.

2.5.10. 1-Phenylethyl acetate 5i (Table 7, entry 9)

IR (KBr) cm^{-1}: 2984, 1725, 1379, 1174, 1062, 698. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.57 (d, J = 25 Hz, 3H), 2.05 (S, 3H), 5.85 (q, J = 25 Hz, 1H), 7.33 (s, 5H) ppm.

2.5.11. Benzhydryl acetate 5j (Table 7, entry 10)

IR (KBr) cm^{-1}: 1742, 1371, 1232, 1022, 698. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 7.06 (S, 1H), 7.45 (s, 10H) ppm.

2.5.12. 4-Methoxyphenyl acetate 5q (Table 7, entry 17)

^1H NMR (250 MHz, $CDCl_3$): δ = 2.23 (S, 3H), 3.74 (S, 3H), 6.94 (m, 4H) ppm.

3. Results and discussion

In continuation of our studies on magnetic nanocatalysts [5–7,26], herein, we report four simple and efficient methods for the application of SSA@MNPs as a magnetically recoverable nanocatalyst in the oxidation of sulfides, acetylation of alcohols

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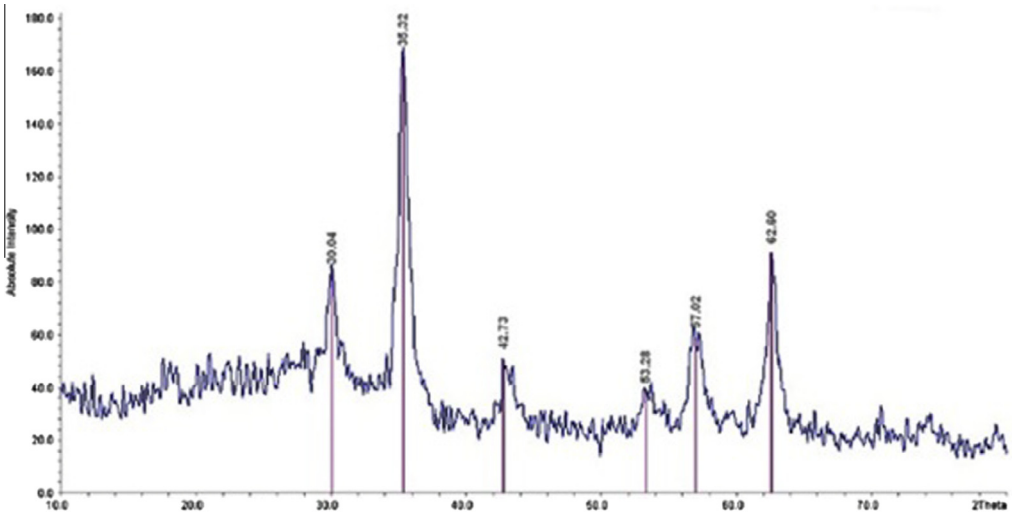


Figure 3 XRD pattern of SSA@MNPs.

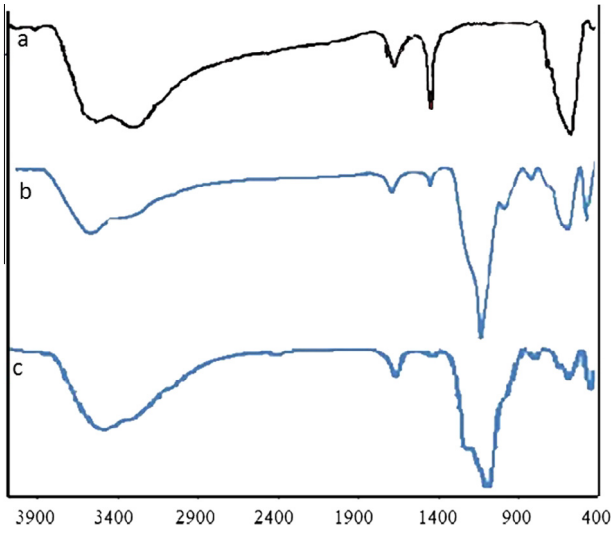
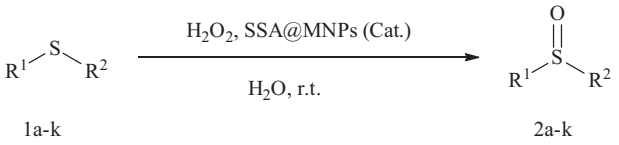


Figure 4 FT-IR spectra of (a) magnetic nanoparticle Fe_3O_4, (b) magnetic nanoparticles coated by silica (SiO_2@MNPs), and (c) silica sulfuric acid-coated Fe_3O_4 nanoparticles (SSA@MNPs).

and phenols, trimethylsilylation of benzylic alcohols and also deprotection of silyl ethers into their corresponding alcohols. All processes were carried out at room temperature and in the presence of catalytic amounts of SSA@MNPs as catalyst.

The details of the supported catalyst preparation procedure are presented in Scheme 1. Initially, the Fe_3O_4 MNPs have been prepared [5–7]. Ultimately, after coating of the Fe_3O_4 MNPs with silica layers (using TEOS), the functionalization of facial hydroxyl groups with chlorosulfonic acid led to SSA@MNPs. The catalyst has been characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), and by their comparisons with those of authentic samples [27–30].

The size of the catalyst was evaluated using SEM. The SEM image of SSA@MNPs shows that the catalyst was formed of nanometer-sized particles (Fig. 1).



Scheme 2 SSA@MNPs catalyzed the oxidation of sulfides into sulfoxides using H_2O_2.

The TGA was also used to determine the percent of functional groups chemisorbed onto the surface of magnetic nanoparticles. The TGA curve of the SSA@MNPs shows the mass loss of the functional group as it decomposes upon heating (Fig. 2). The weight loss at temperatures below 200 °C is due to the removal of physically adsorbed solvent and surface hydroxyl groups. The weight loss of about 2% between 260 and 350 °C may be associated with the thermal crystal phase transformation from Fe_3O_4 to γ-Fe_2O_3 [29] and decomposition of sulfuric acid and formation of sulfur dioxide [22]. Silica sulfuric acid groups have been reported to desorb at temperatures above 260 to more than 600 °C. On the basis of these results, the well grafting of sulfuric acid on Fe_3O_4 is verified.

The XRD spectrum of SSA@MNPs is shown in Fig. 3. As seen in Fig. 3, SSA@MNPs display six characteristic peaks at the 2θ values of 30.04, 35.32, 42.73, 53.28, 57.02 and 62.90 [30]. The position and relative intensities of all peaks agree well.

Fig. 4 shows the FT-IR spectra of Fe_3O_4, SiO_2@MNPs and SSA@MNPs. The Fe–O stretching vibration by two strong absorption bands at near 580 and 440 cm^{-1}, symmetrical and asymmetrical modes of the O–H bond stretching vibration near 3418 and 3550 cm^{-1} and O–H deformed vibration near 1650 cm^{-1} were observed in FT-IR spectrum of bare Fe_3O_4 MNPs [5]. Several peaks in FT-IR spectrum of SSA@MNPs at 640, 1220, 1230 and 2800–3700 cm^{-1} can be attributed to the characteristic absorption of sulfonic acid groups. The introduction of silica and silica sulfuric acid on the surface of MNPs is confirmed by the band at about 1000 cm^{-1} assigned to the Fe–O–Si stretching vibrations. Also, in the 500–700 cm^{-1} spectral region of the FT-IR spectra, an overlap

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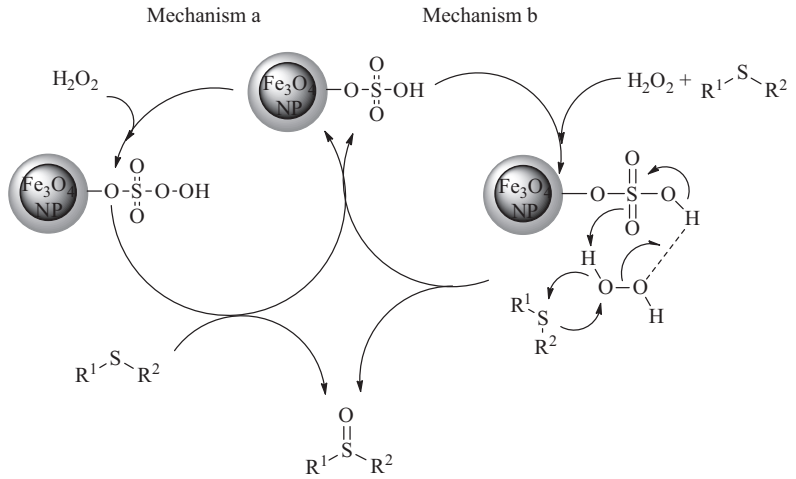

Scheme 3 Proposed mechanisms for the oxidation of sulfides using H_2O_2 in the presence of SSA@MNPs as catalyst.

Scheme 4 SSA@MNPs catalyzed the trimethylsilylation of hydroxyl groups and also, deprotection of silyl ethers into their corresponding alcohols.

of the stretching vibrations of the Fe–O bonds with the S–O bond in the sulfonic acid group stretching vibration modes as a weak band leads to band broadening [30].

As a first part of our ongoing program, we tested the catalytic activity of SSA@MNPs in the oxidation of sulfides into corresponding sulfoxides using H_2O_2 (Scheme 2).

For the optimization of the reaction conditions, we examined the oxidation of benzyl methyl sulfide using H_2O_2 in various solvents and in the presence of different amounts of catalyst (Table 1). As shown in Table 1, benzyl methyl sulfide (1 mmol) in the presence of SSA@MNPs (0.005 g) in water at room temperature was found to be ideal under the reaction conditions for the formation of benzyl methyl sulfoxide.

The generality of this approach has been demonstrated by a facile oxidation of various sulfides as shown in Table 2. The sulfoxides were obtained in high yields. As shown, a variety of sulfides were successfully employed to prepare the corresponding sulfoxides. Therefore, the results revealed that this methodology is effective for a wide range of sulfides.

The possible mechanistic path for the oxidation of sulfides is shown in Scheme 3 [26], one explanation for this transformation is the in-situ formation of peroxyacid using the reaction of SSA@MNPs with H_2O_2, followed by the oxygen transfer to the organic substrate (Scheme 3a). Another explanation is that SSA@MNPs act as protic acid, which polarizes the O–O bond in hydrogen peroxide to produce the reactive oxygen transfer agent (Scheme 3b).

Figure 5 Image showing SSA@MNPs can be separated by applied magnetic field. A reaction mixture in the absence (left) or presence of a magnetic field (right).

In the second part of our study, we reported the catalytic activity of SSA@MNPs in the selective trimethylsilylation of benzylic alcohols in acetonitrile at room temperature. Also, deprotection of silyl ethers was reported in ethanol at room temperature in the presence of SSA@MNPs (Scheme 4).

For the optimization of the reaction conditions, we studied the reaction of benzyl alcohol with HMDS in a variety of solvents and different amounts of SSA@MNPs (Table 3). As shown in Table 3, CH_3CN was used as the solvent and also

Scheme 5 SSA@MNPs catalyzed the acetylation of hydroxyl groups using Ac_2O at room temperature.

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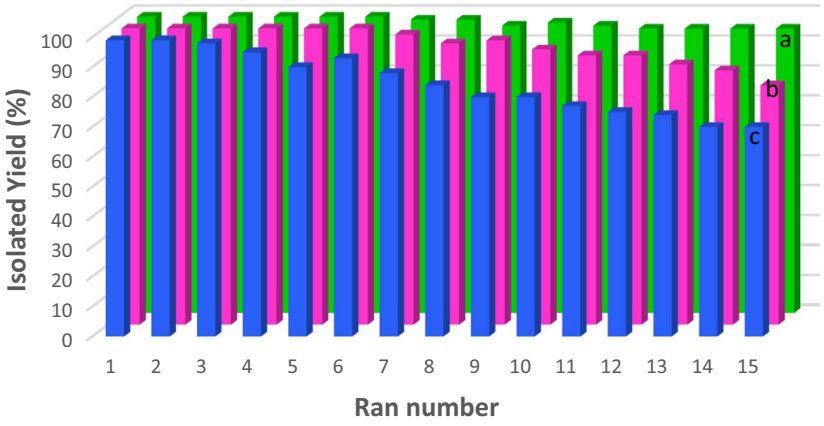

Figure 6 Recycling experiment of SSA@MNPs (0.005 g) in the (a) trimethylsilylation of benzyl alcohol, (b) acetylation of benzyl alcohol and (c) oxidation of methyl phenyl sulfide in the influence of SSA@MNPs.

we found that 0.005 g of SSA@MNPs was sufficient to catalyze the reaction. Under this conditions, a variety of benzylic alcohols including several functional groups are efficiently converted to their corresponding trimethylsilyl ethers, while the protection of primary and secondary aliphatic alcohols was not observed or barely reactive.

In continuation of our studies on the application of SSA@MNPs in organic transformation, we report an efficient method for the deprotection of silyl ethers and converting into parent hydroxyl groups as shown in Scheme 3. The result of this study is shown in Table 5.

In the final part of our studies, we report the use of SSA@MNPs as a highly efficient catalyst for the acetylation of hydroxyl groups using Ac_2O at room temperature. The features of these reactions are outlined in Scheme 5.

For the optimization of the reaction conditions, acetylation of benzyl alcohol was conducted in different solvents and in the presence of different amounts of catalyst and Ac_2O at room temperature (Table 6). As shown in Table 6, we chose 0.005 g of catalyst and 1.5 mmol of Ac_2O under solvent-free reaction conditions.

In order to explore the activity of the catalyst, various hydroxyl groups including primary and secondary alcohols and phenols with electron donating and electron withdrawing groups were acetylated in the presence of SSA@MNPs under optimized conditions and the corresponding acetate compounds were obtained in good to excellent yields (Table 7).

We have found that this catalyst recovered rapidly and demonstrated remarkably excellent recyclability; to investigate this issue, the recyclability of the catalyst was examined in the oxidation of methyl phenyl sulfide, trimethylsilylation and acetylation of benzyl alcohol. After the completion of the reaction, the catalyst was separated by an external magnet (Fig. 5). The remaining magnetic nanocatalyst was reused under similar reaction conditions. As shown in Fig. 6, the catalyst was reusable without any significant loss of activity for the 15th recycling.

4. Conclusions

In conclusion, simple, efficient and environmentally benign methods have been developed for the oxidation of sulfides, acetylation of alcohols and phenols and selective trimethylsilylation of primary and secondary benzyl alcohols in the presence of SSA@MNPs having high catalytic activity. The advantages of these protocols are the use of a commercially available, eco-friendly, cheap and chemically stable reagents, with operational simplicity, practicability and good to high yields. The separation of products and recycling of catalysts are easier and simpler with the assistance of an external magnet. The catalyst can be reused 15 times with little loss of activity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jscs.2015.07.007.

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